

# Electrochemistry for materials technology

## Chapter 7

Experimental study of electrochemical reactions

*(D. Landolt, Corrosion and Surface chemistry of  
metals, Chapter 5)*

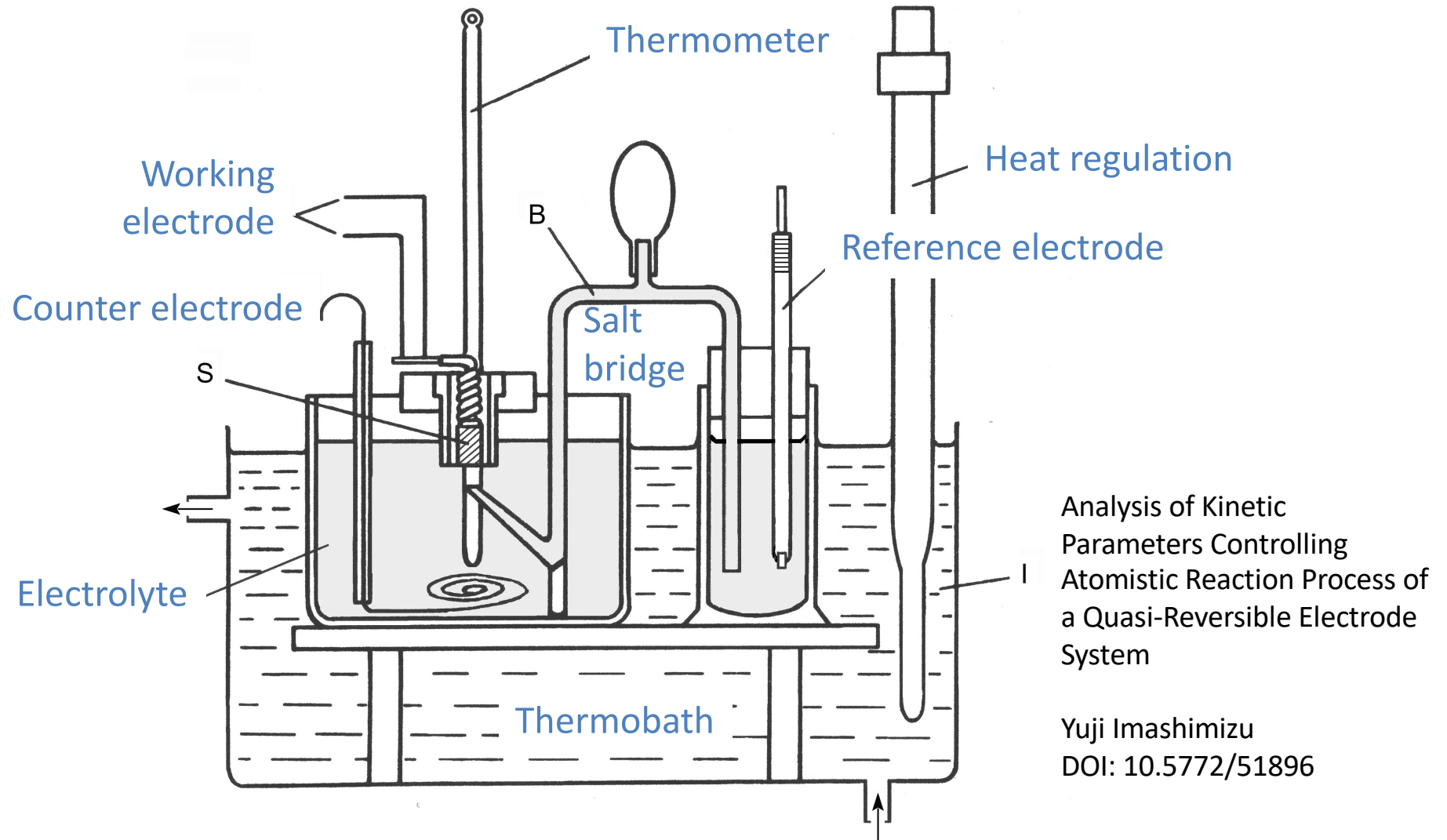
# Content

1. Polarisation measurements
2. Double layer capacitance (galvanostatic impulsion)
3. Potentiostatic impulsion (Cottrell)
4. Electrochemical Impedance Spectroscopy (EIS)
5. Cyclic voltammetry

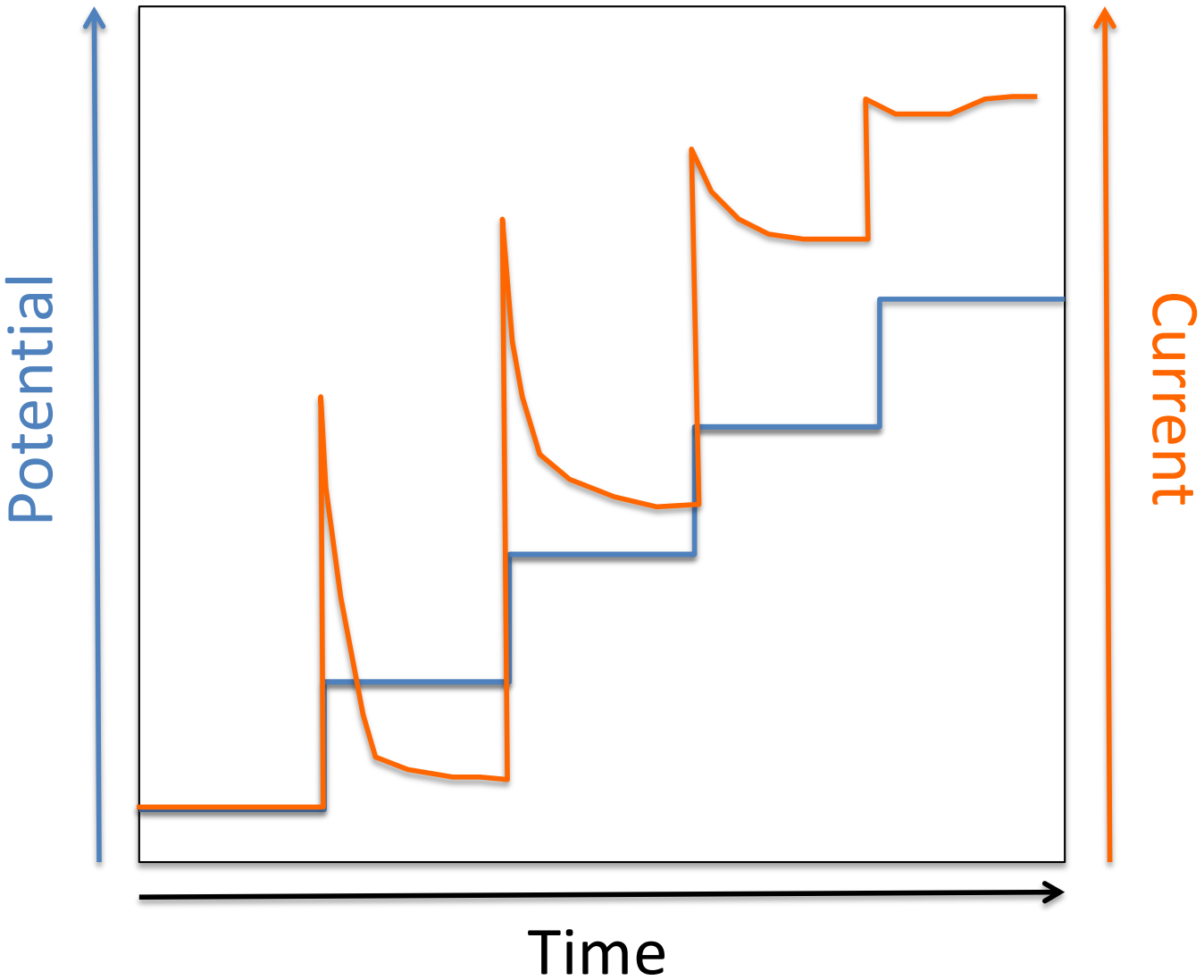
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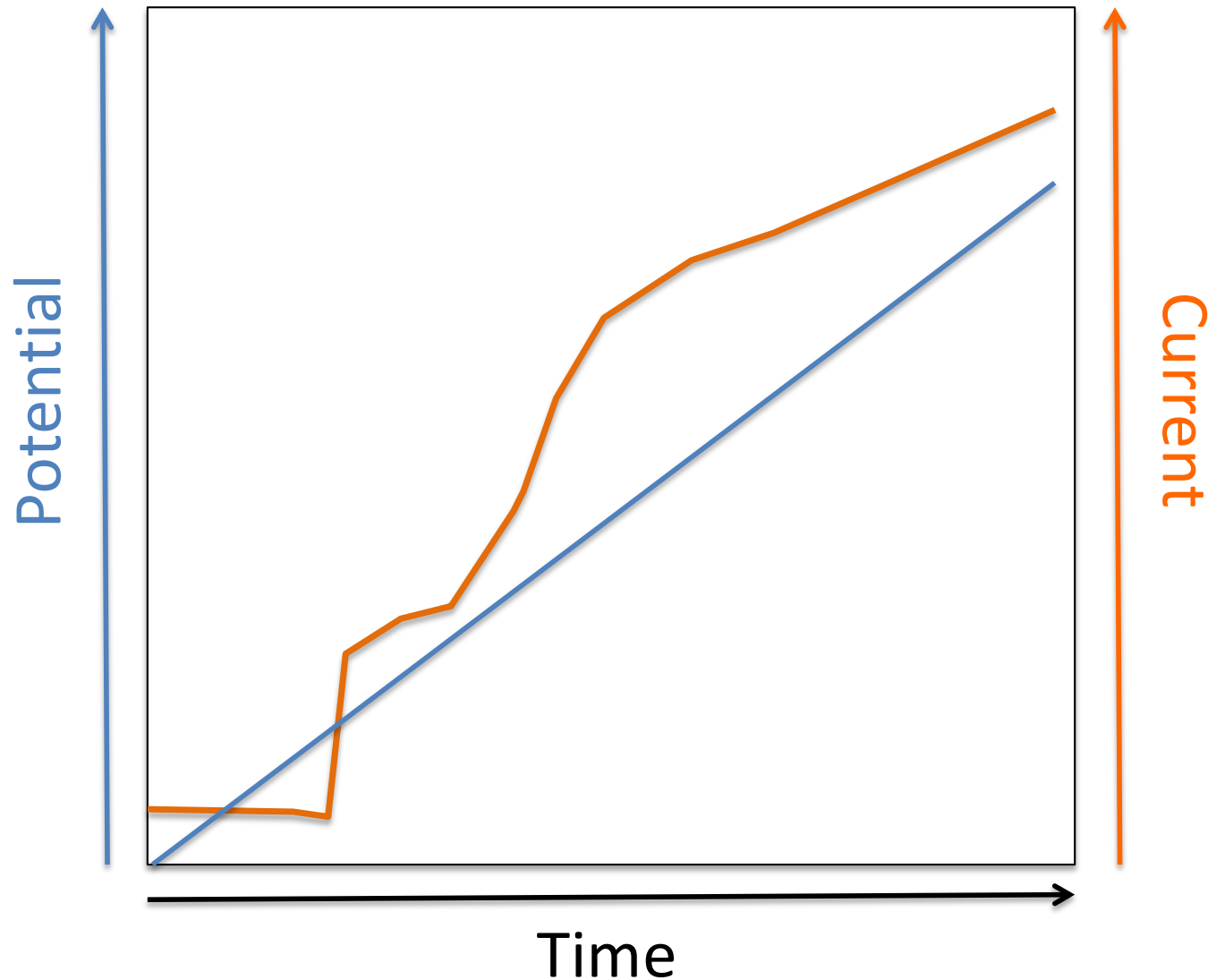
# Schematic diagram of an electrolytic cell for polarisation experiments



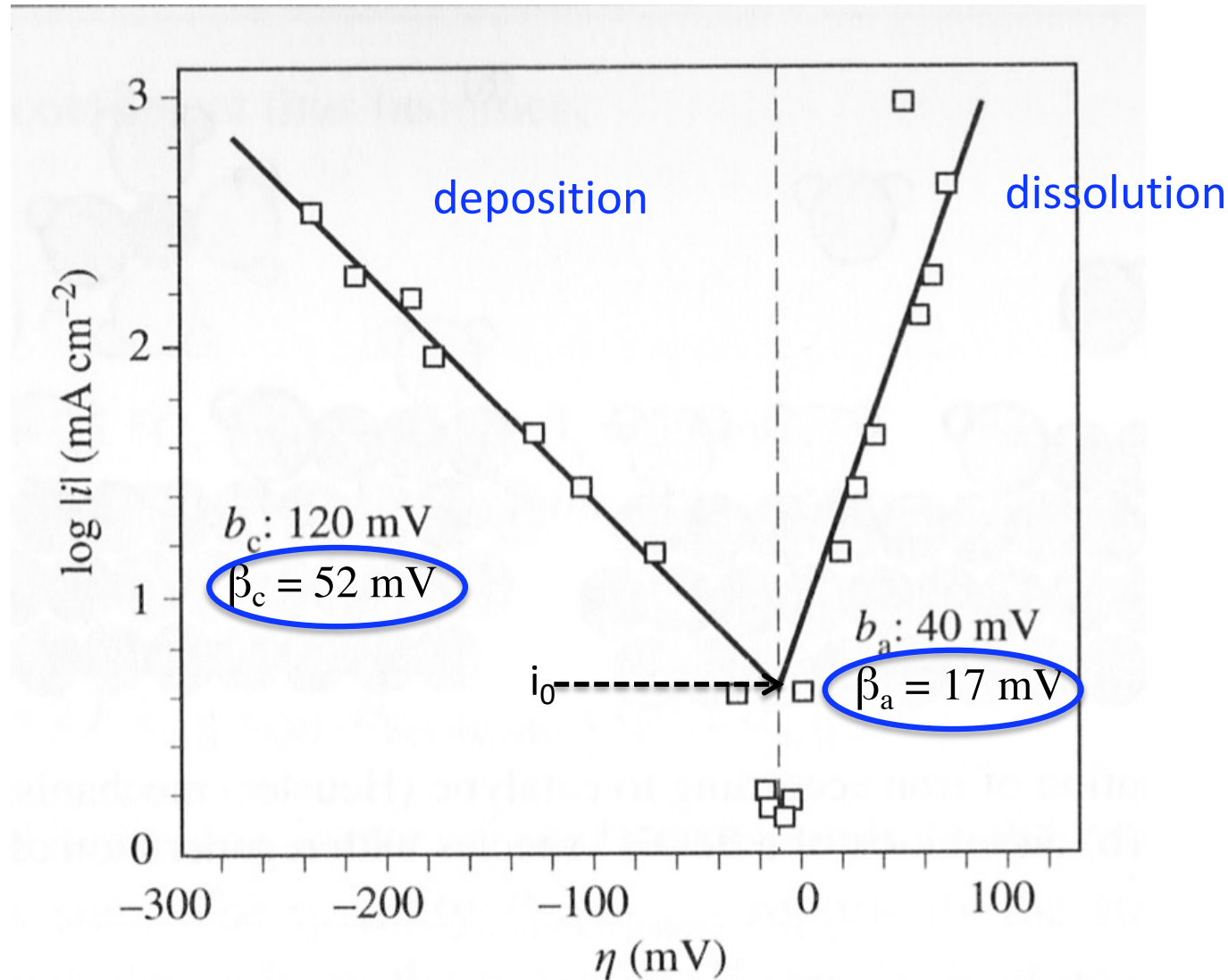
# Principle of potentiostatic polarisation experiments



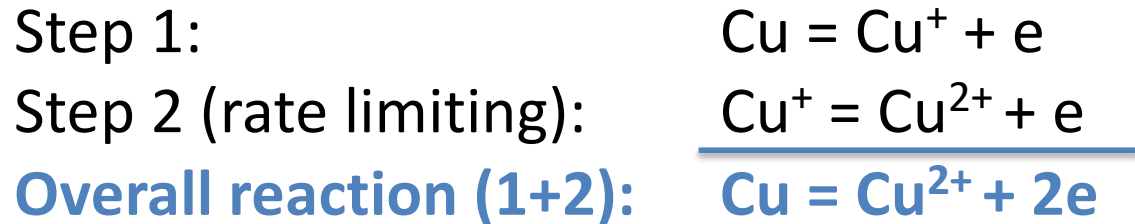
# Principle of potentiodynamic polarisation experiments



# Polarisation curve of copper in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.075 M CuSO<sub>4</sub>



# Mechanisms of copper redox reaction



Butler-Volmer:

$$i_1 = n F k_{a,1} \exp(F \alpha_{a,1} \eta / R T) - n F k_{c,1} a_{\text{Cu}^+} \exp(-F \alpha_{c,1} \eta / R T)$$

$$i_2 = n F k_{a,2} a_{\text{Cu}^+} \exp(F \alpha_{a,2} \eta / R T) - n F k_{c,2} a_{\text{Cu}^{2+}} \exp(-F \alpha_{c,2} \eta / R T)$$

**Step 1 is at equilibrium  $\rightarrow i_1 = 0 \rightarrow a_{\text{Cu}^+} = K_1 \exp(F\eta/R T)$        $K_1 = k_{a,1} / k_{c,1}$**

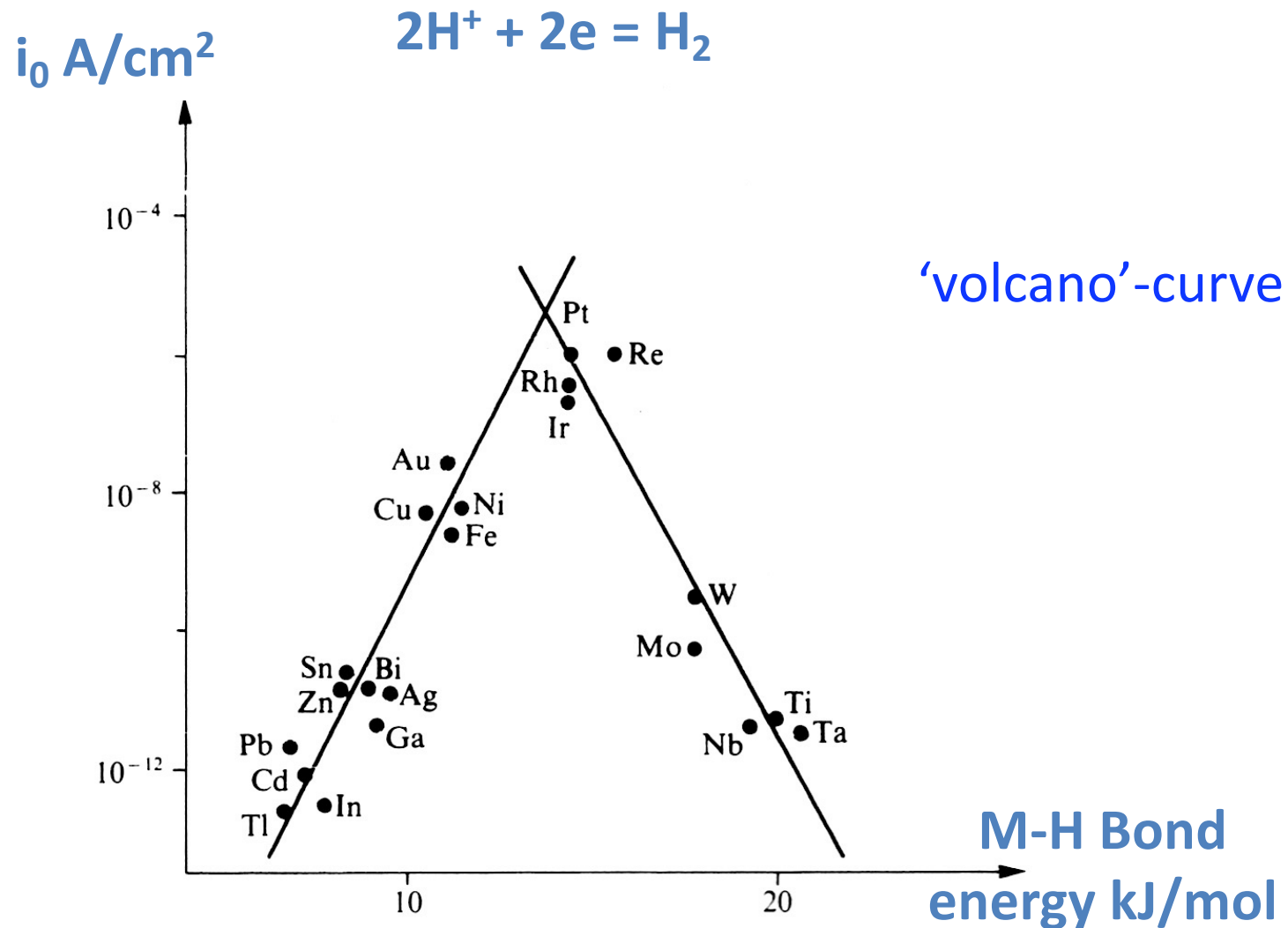
$$i_{a,2} = n F k_{a,2} K_1 \exp(F (1+\alpha_{a,2}) \eta / R T)$$

$$i_{c,2} = n F k_{c,2} a_{\text{Cu}^{2+}} \exp(-F \alpha_{c,2} \eta / R T)$$

$$\beta_a = d \eta / d \ln i_{a,2} = RT / ((1+\alpha_{a,2})F) = 17 \text{ mV for } \alpha=0.5$$

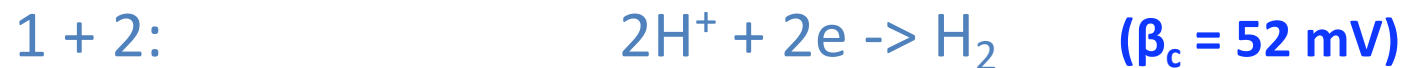
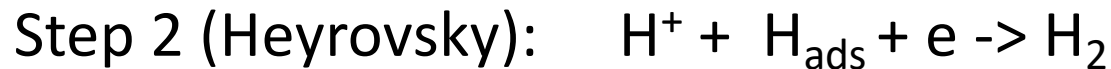
$$\beta_c = d \eta / d \ln i_{c,2} = RT / ((1-\alpha_{c,2})F) = 52 \text{ mV for } \alpha=0.5$$

# Exchange current $i_0$ of hydrogen half cell on different metals M

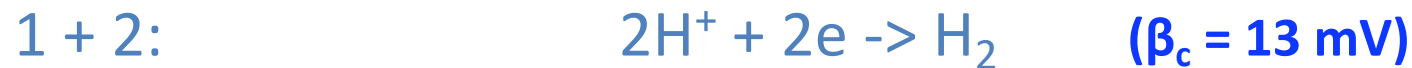
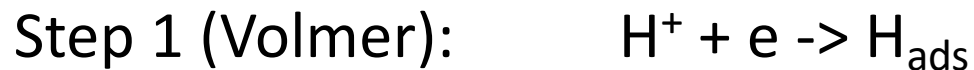


# Reaction mechanisms hypotheses for proton reduction to hydrogen

Volmer-Heyrovsky mechanism (for low coverage  $H_{ads}$ ):



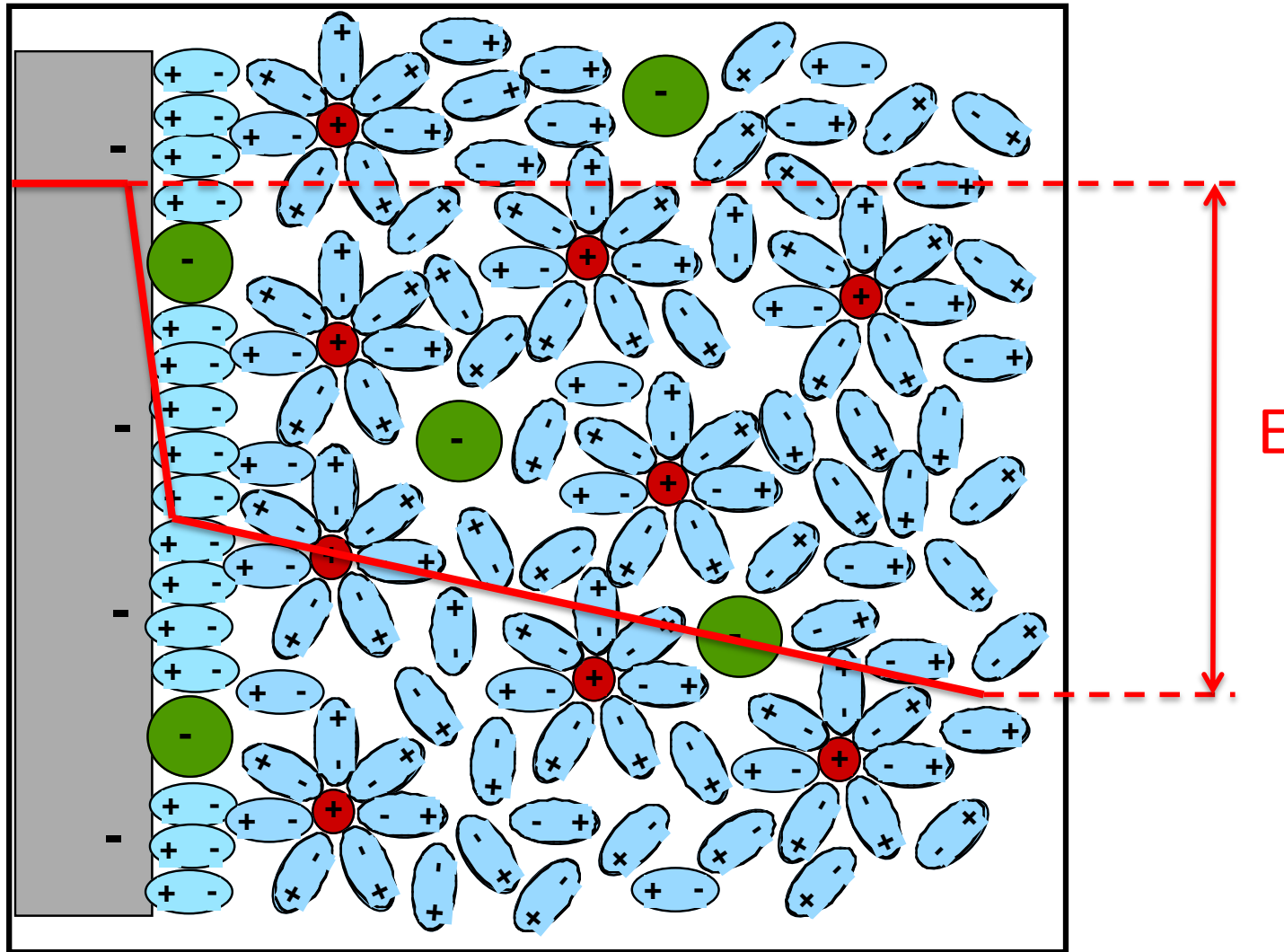
Volmer-Tafel mechanism (at high coverage  $H_{ads}$ ):



# Content

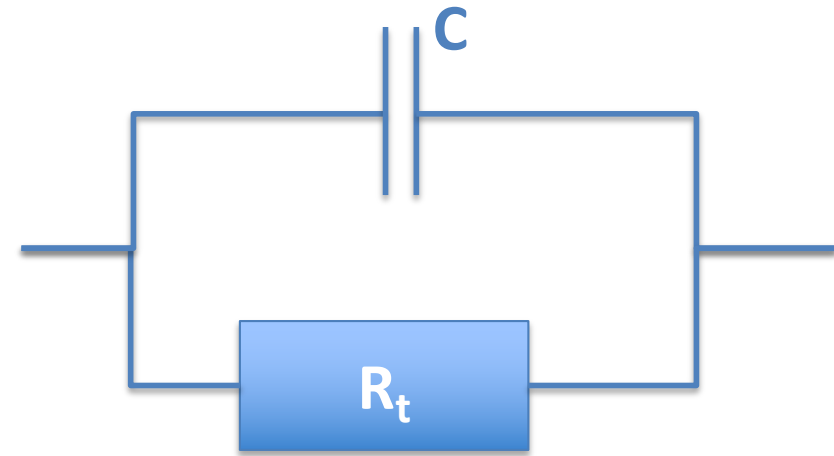
1. Polarisation measurements
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# Electrical double layer at metal-electrolyte interface



# Equivalent circuit of metal-electrolyte interface

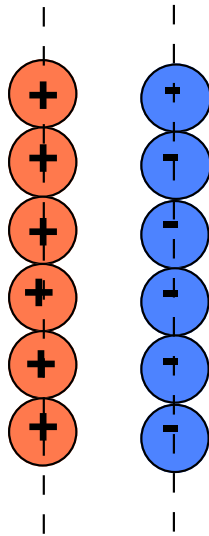
Electrode with double layer capacitance «  $C$  » and charge transfer resistance «  $R_t$  »



Ideally polarizable electrode, i.e. with infinite charge transfer resistance  $R_t$ .



# Helmholtz model of electrical double layer



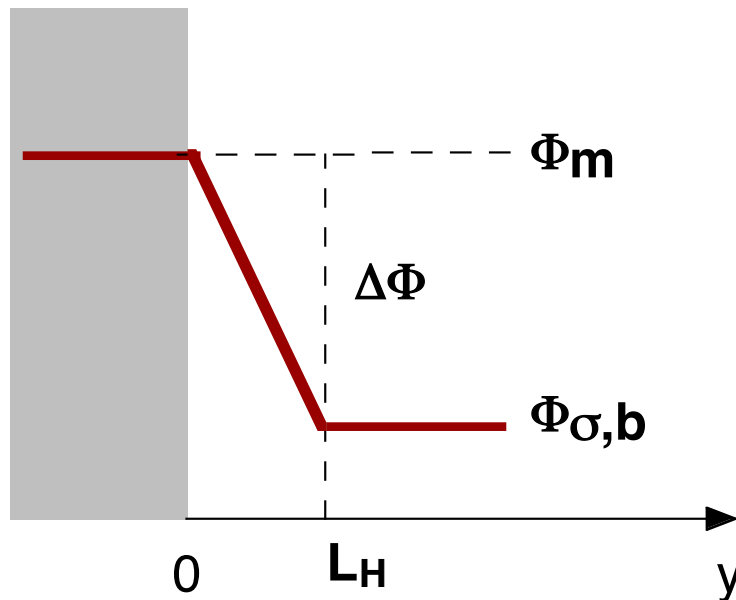
$$C_H = \frac{\epsilon \epsilon_0}{L_H}$$

$C_H$ : double layer capacitance

$\epsilon$  : dielectric constant of the solvent

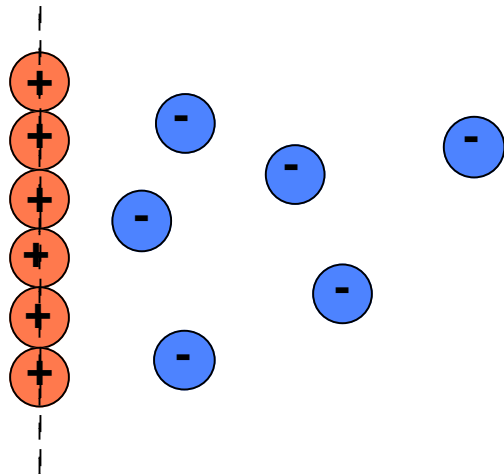
$\epsilon_0$  : permittivity constant

$L_H$  : thickness of the double layer



*For  $L_H = 0.5 \text{ nm}$  and  $\epsilon_{H_2O} = 78$ ,  
 $C_H$  corresponds to  $70 \mu\text{F}/\text{cm}^2$*

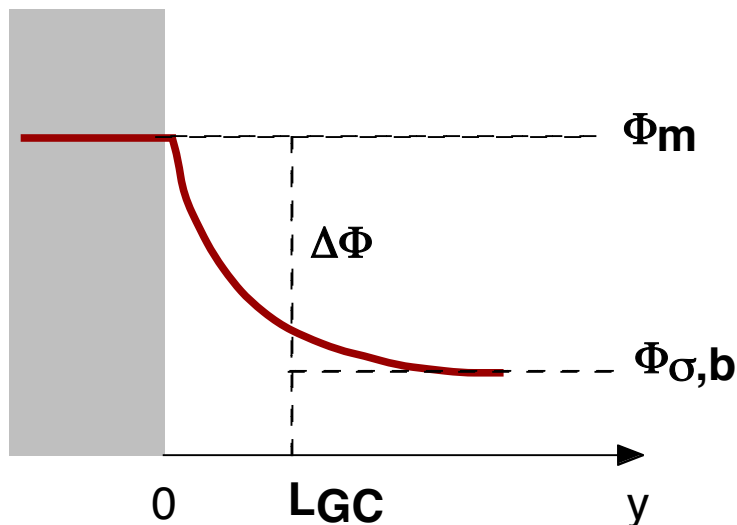
# Gouy-Chapman model of electrical double layer (binary electrolyte, e.g. NaCl)



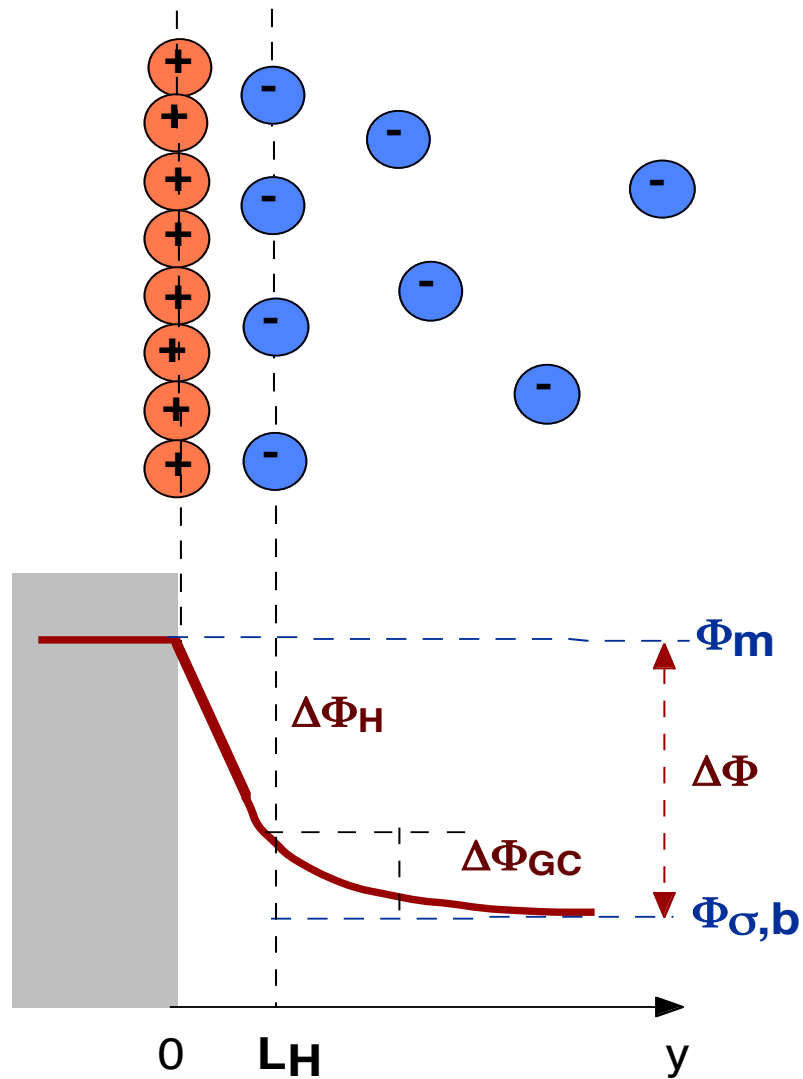
$$C_{GC} = \frac{\varepsilon \varepsilon_0}{L_{GC}} \cosh\left(\frac{zF\Delta\Phi}{2RT}\right)$$

$$L_{GC} = \left(\frac{\varepsilon \varepsilon_0^2 RT}{2 z^2 F^2 c_b}\right)^{0.5}$$

$c_b$  : salt concentration  
 $z$  : ions charge



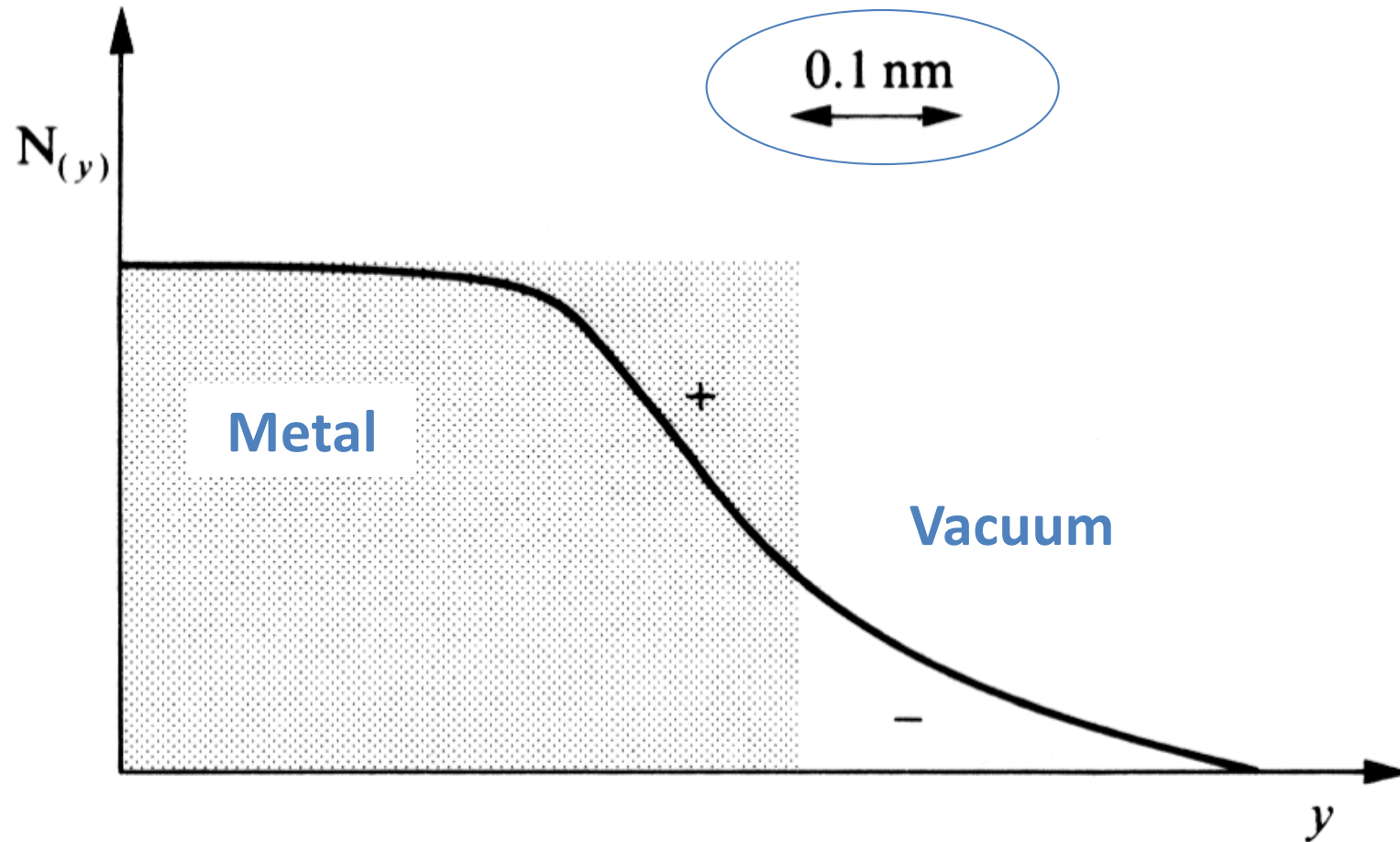
# Stern model of electrical double layer



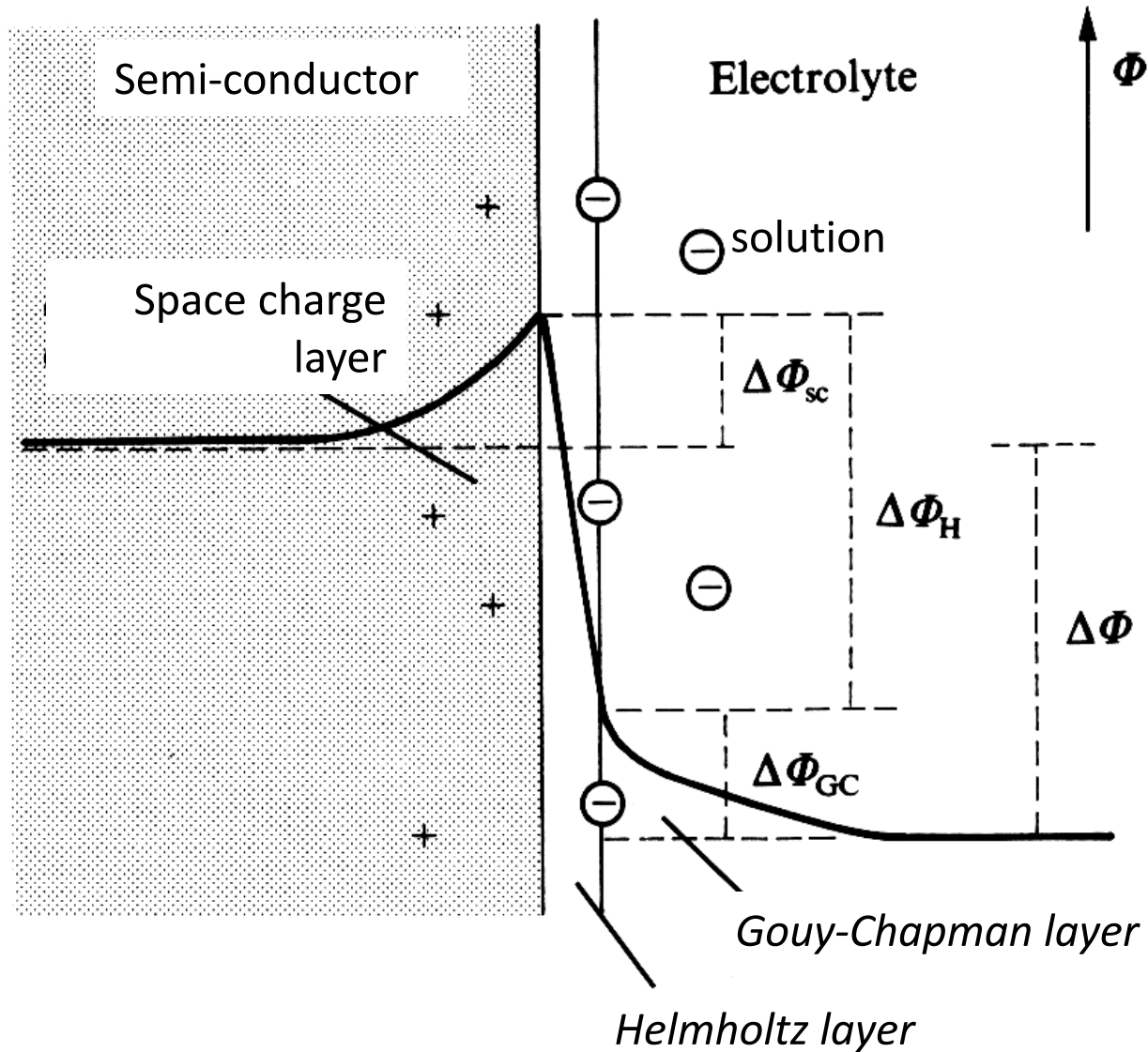
$$C^{-1} = C_H^{-1} + C_{GC}^{-1}$$

series connection of Helmholtz  
and Gouy-Chapman capacitances

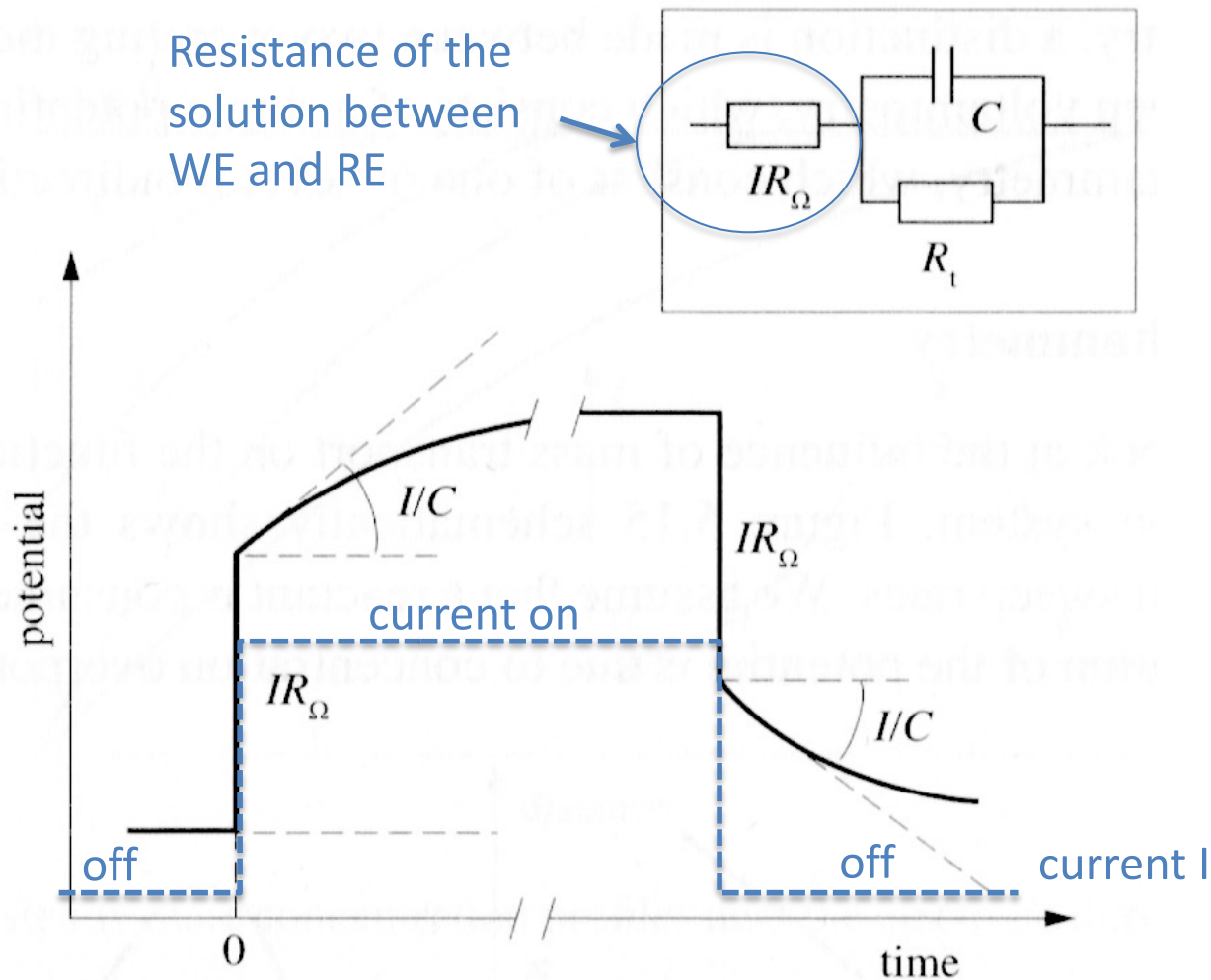
# Electron density variation with distance at metal-vacuum interface



# Double layer at semiconductor-electrolyte interface



# Measurement of double layer capacitance $C_{dl}$ by galvanostatic transient method (switching current $i$ on/off)

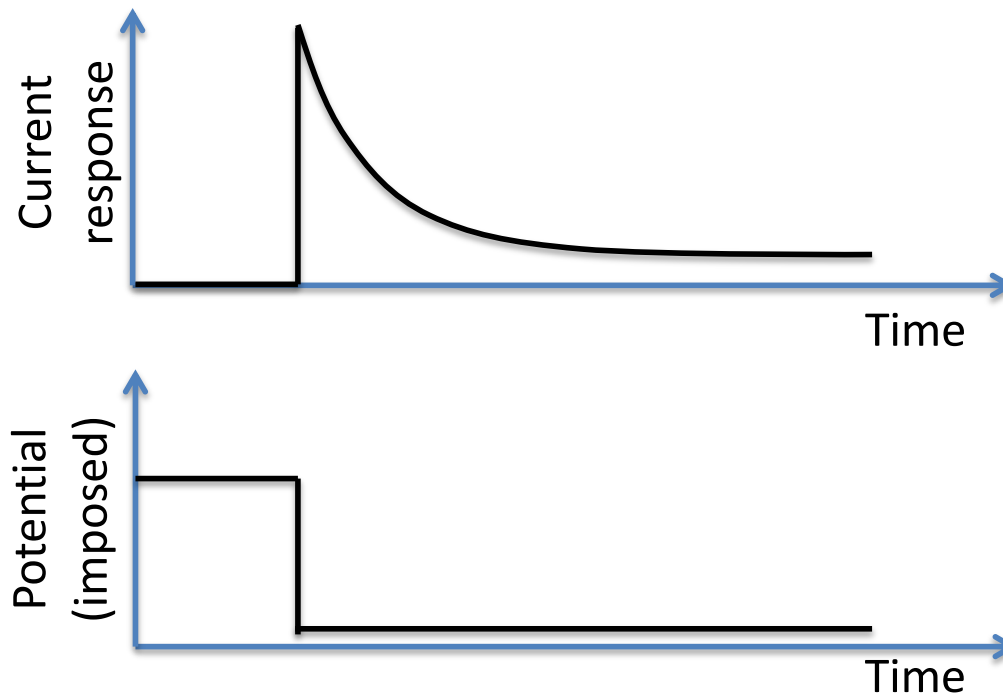


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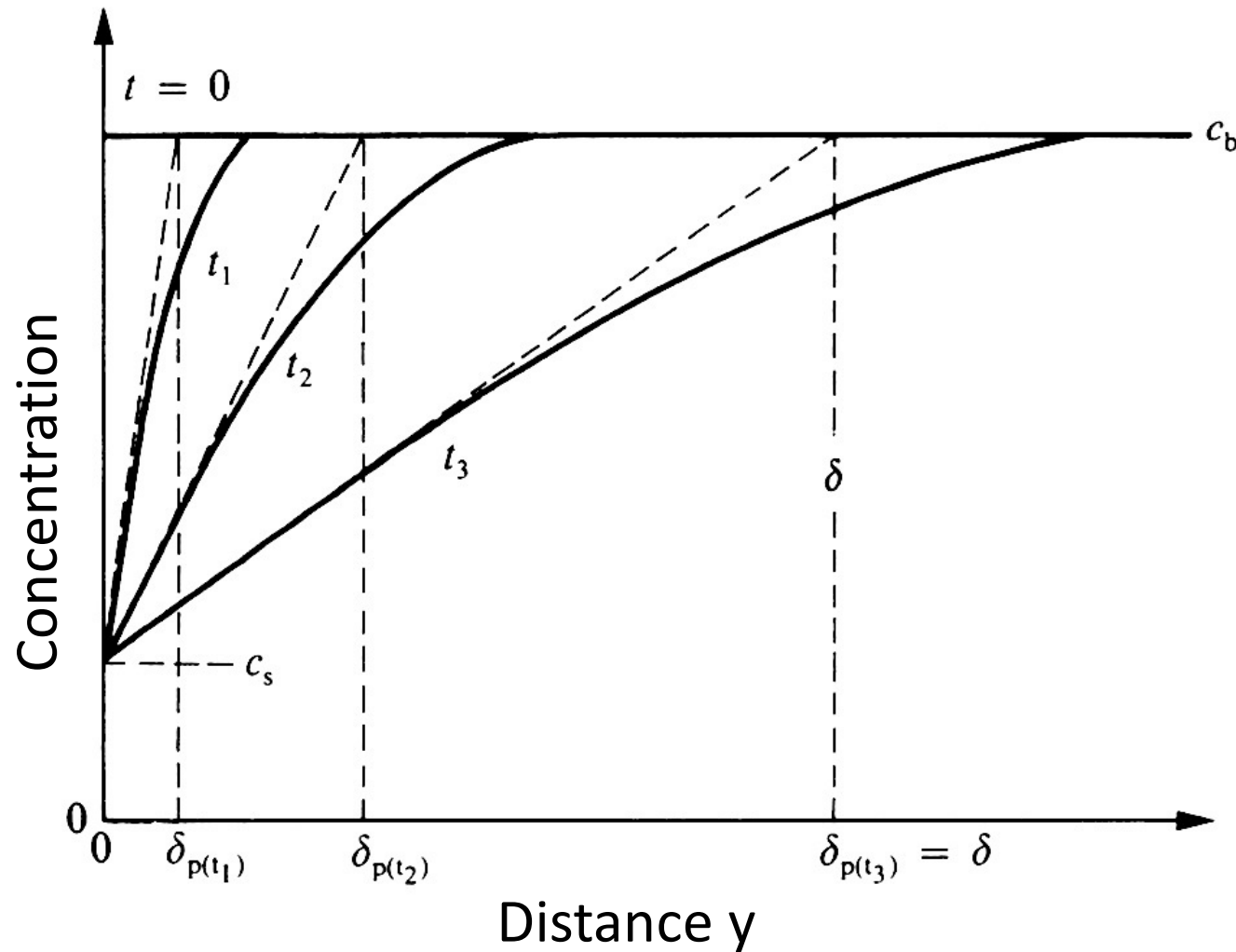
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# Cottrell equation (diffusion control)

Cottrell's equation describes the evolution of current with time during a potential step in case of a **mass transport limited** electrode reaction (e.g. metal deposition)



# Concentration profiles near the electrode after potential step



$\delta$ : thickness of the steady state diffusion layer

$\delta_p$ : thickness of the non steady state diffusion layer

$c_b, c_s$ : concentration of reacting species at the surface (s) and in the bulk (b).

# Current density for non-steady state concentration profiles

Case of the cathodic reduction of a species at the electrode:

$$i_c = - n F \left. \frac{d c}{d y} \right|_{y=0} \quad \text{mass transport controlled kinetics, Fick's 1st Law}$$

$$\frac{d c}{d t} = D \frac{d^2 c}{d y^2} \quad \text{concentration evolution with time, Fick's 2nd Law}$$

Solving the above equation system yields the **Cottrell equation**:

$$i_c = - n F (c_b - c_s) (D/(\pi t))^{0.5}$$

in practice : plot  $i$  vs  $1/\sqrt{t}$ ;

when the result is linear, the reaction is diffusion-controlled

# Cottrell equation and transition time from non-steady state to steady state diffusion layer

Cottrell equation:

$$i_c = -n F (c_b - c_s) (D/(\pi t))^{0.5}$$

Introducing the non-steady state diffusion layer  $\delta_p$

$$\delta_p(t) = (D \pi t)^{0.5}$$

$$i_c = -n F (c_b - c_s) D / \delta_{p(t)}$$

Steady state when  $\delta_p(t) = \delta$

Transition time  $t_{tr}$  from non-steady state to steady state

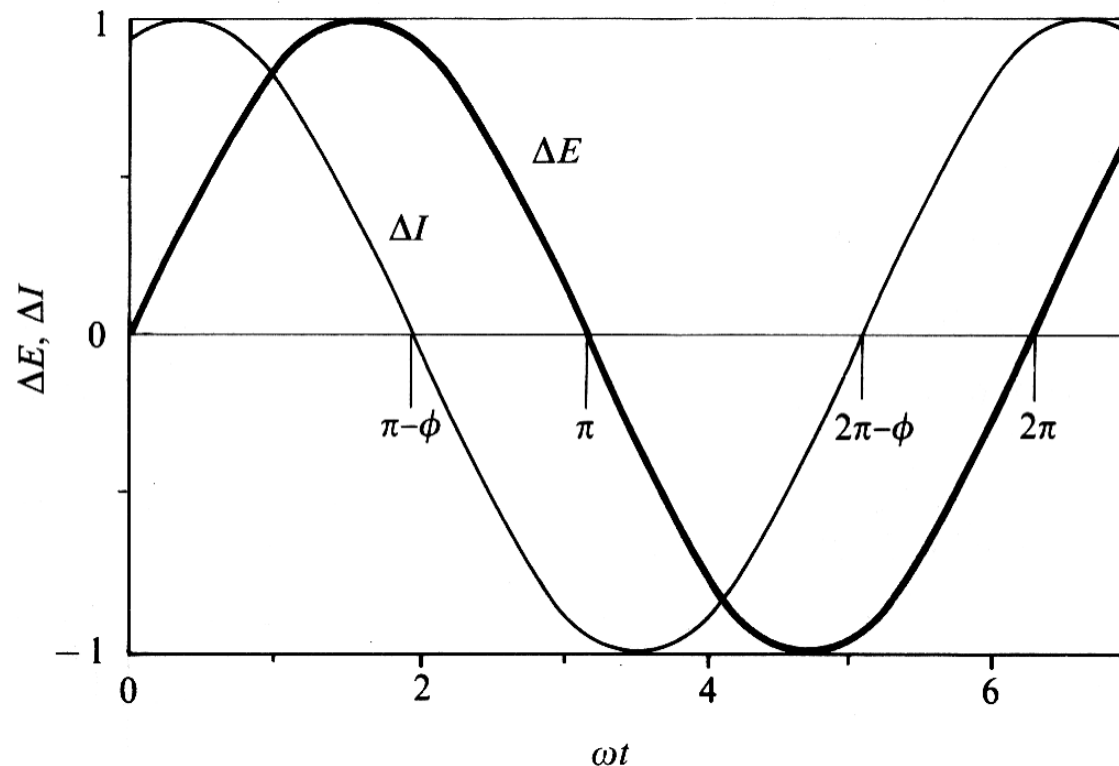
$$t_{tr} = \delta^2 / D \pi$$

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# Principle of Electrochemical Impedance Spectroscopy (EIS)

An *ac* voltage (typically  $\pm 10$  mV) with frequencies ranging from MHz to mHz is added to an imposed (*dc*) potential. The *ac* potentials and current responses are then passed to a frequency response analyzer (FRA) to calculate the impedance and phase shift.



# Electrochemical Impedance

$\omega = 2 \pi f$  angular frequency where  $f$  is the AC frequency

$E_t = E_0 \sin(\omega t)$  potential vs time

$I_t = I_0 \sin(\omega t + \phi)$  current vs time

Impedance  $Z$

$$Z = E_t / I_t = Z_0 \sin(\omega t) / \sin(\omega t + \phi)$$

# Impedance in the complex plane

$$\exp(j\phi) = \cos\phi + j\sin\phi \quad \text{Euler's relationship}$$

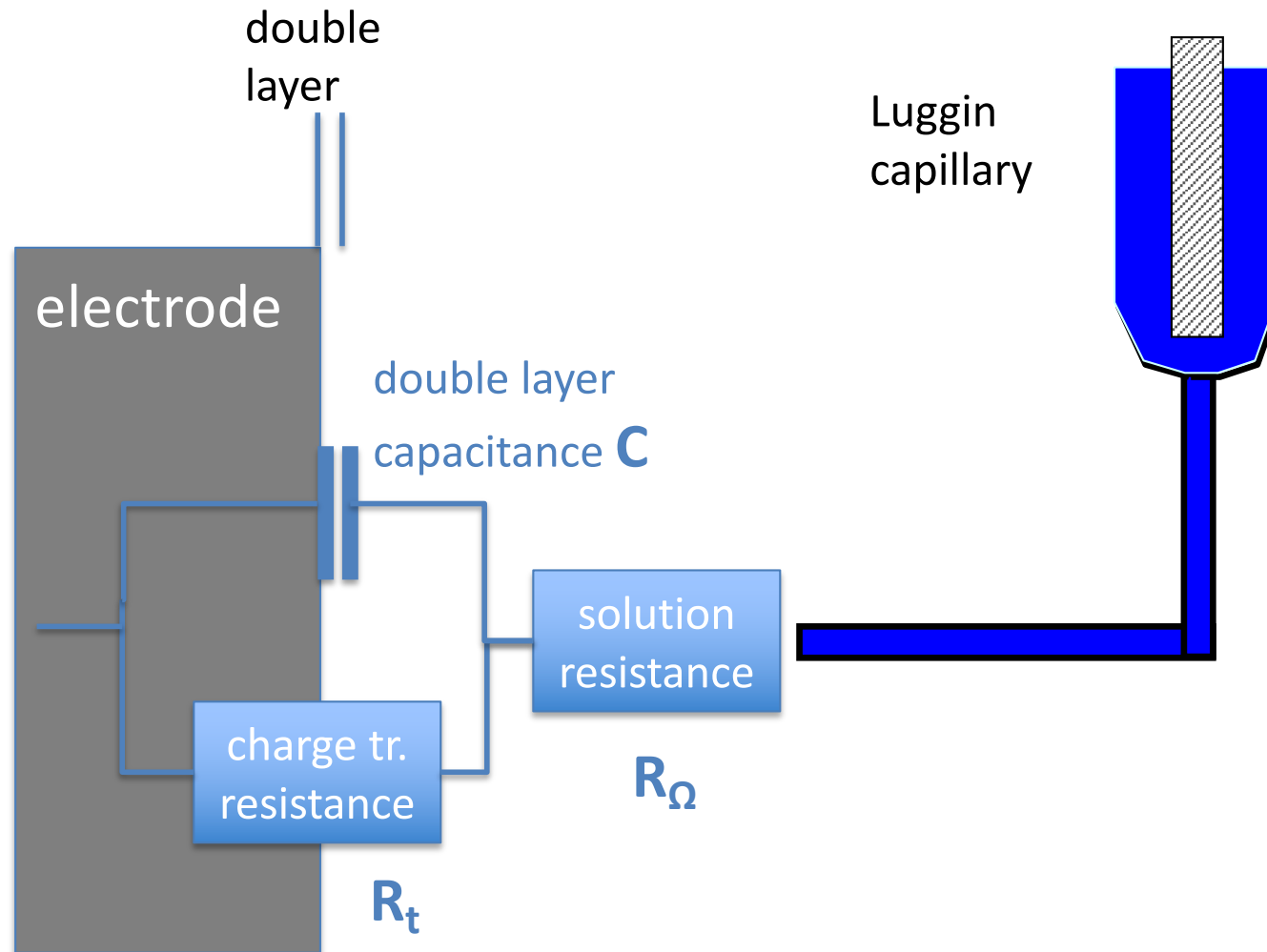
$$E_t = E_0 \exp(j\omega t)$$

$$I_t = I_0 \exp(j\omega t - \phi)$$

Impedance  $Z$

$$Z(\omega) = E_t / I_t = Z_0 \exp(j\phi) = Z_0 (\cos\phi + j\sin\phi)$$

# Electrochemical interfaces and equivalent circuits



# Impedance of some electrical elements

Resistance:

$$Z_{re} = R$$

$$Z_{im} = 0$$

Capacitance

$$Z_{re} = 0$$

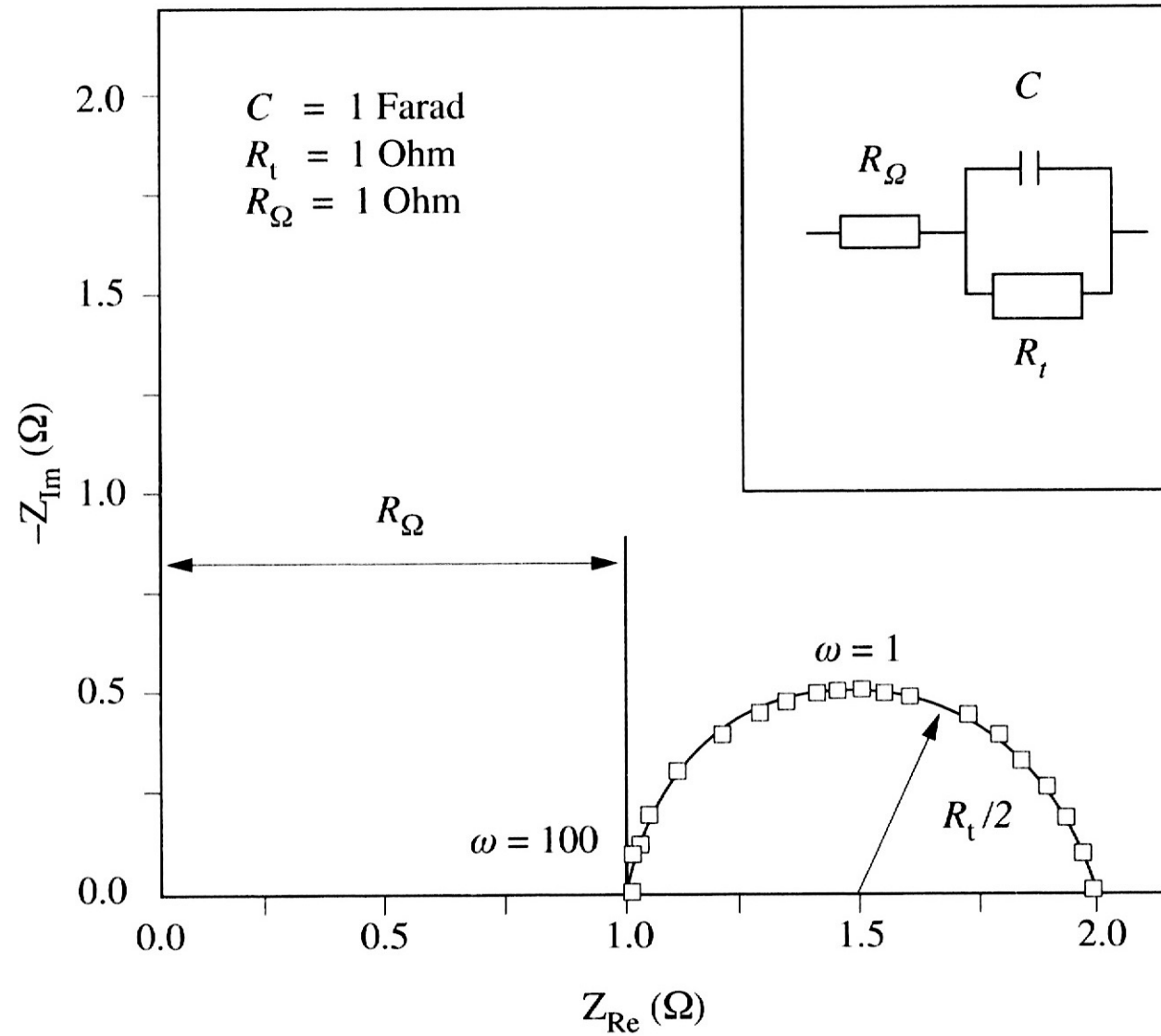
$$Z_{im} = -j/\omega C$$

Inductance

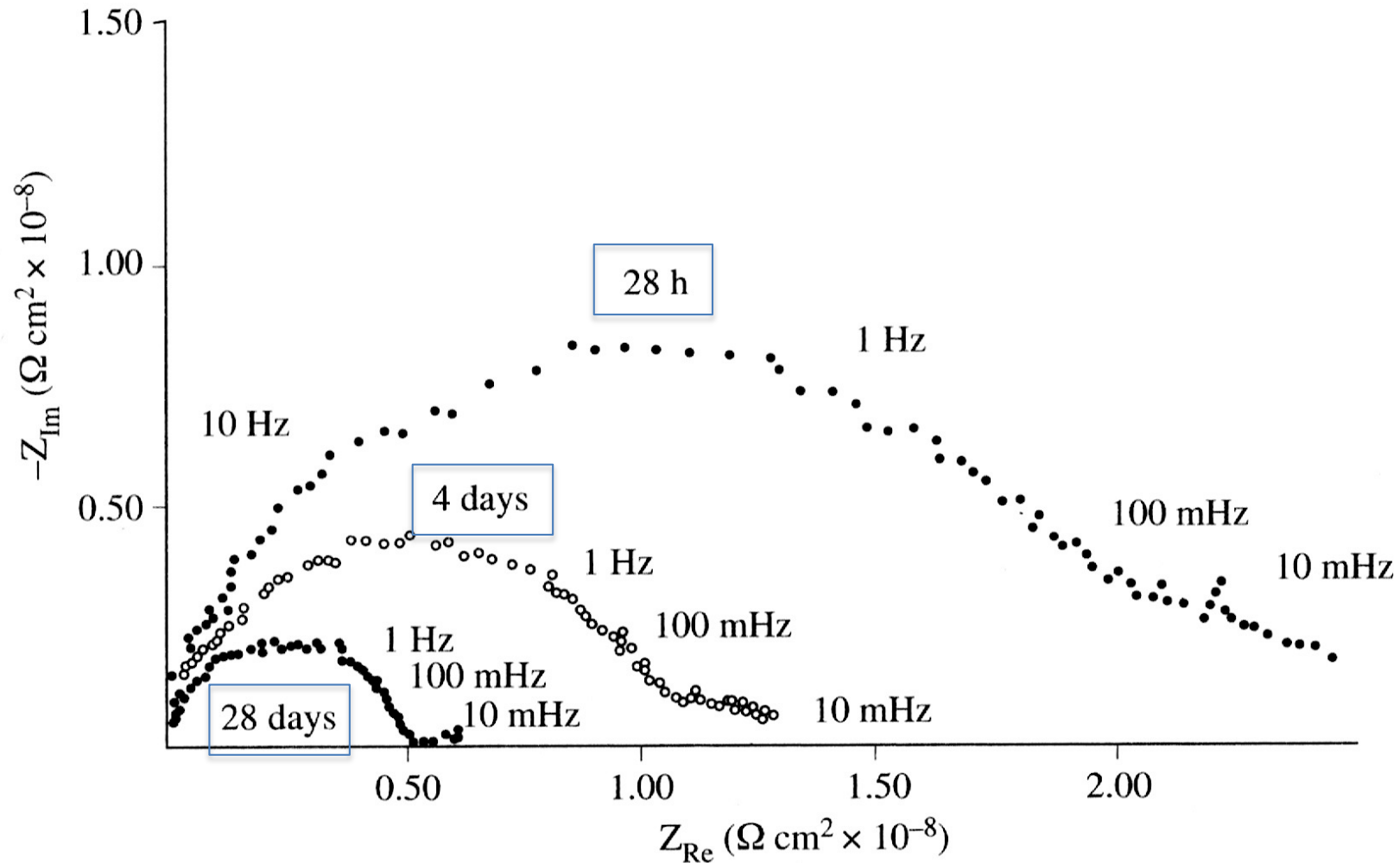
$$Z_{re} = 0$$

$$Z_{im} = -j \omega L$$

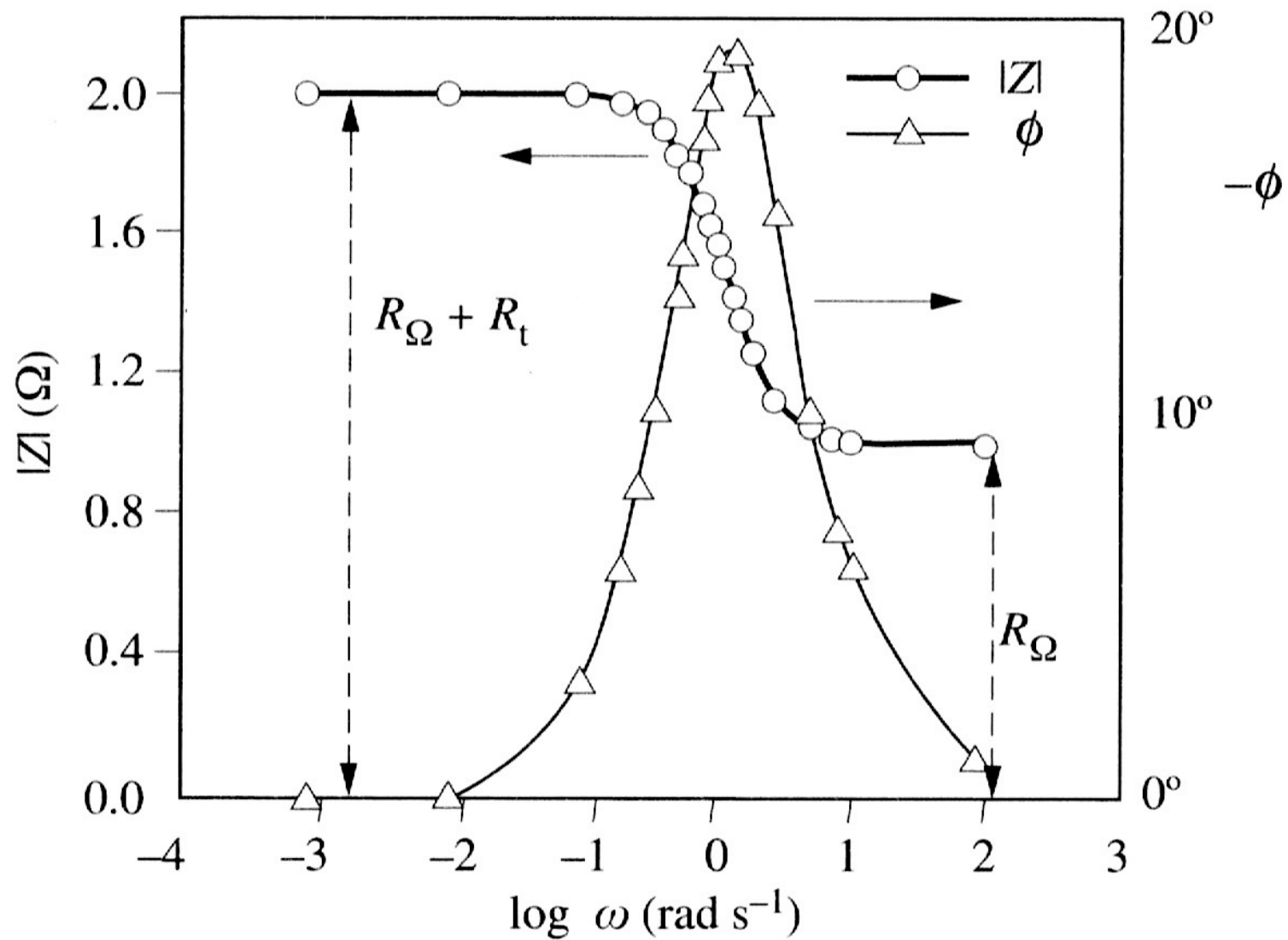
# Nyquist plot



# Nyquist diagram of a paint-coated steel vs exposure time to NaCl solutions



# Bode plot



# Bode plot for a passivating metal electrode at different immersion times

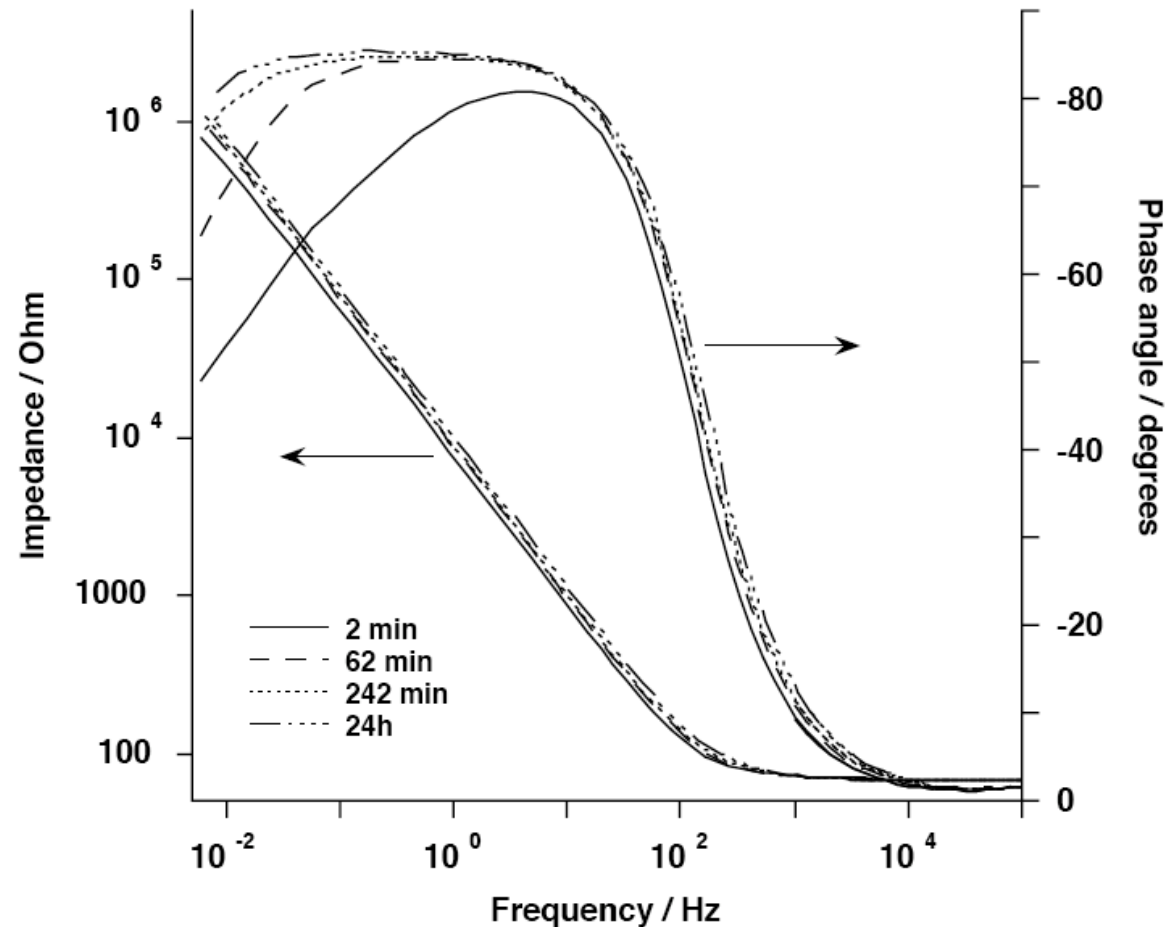
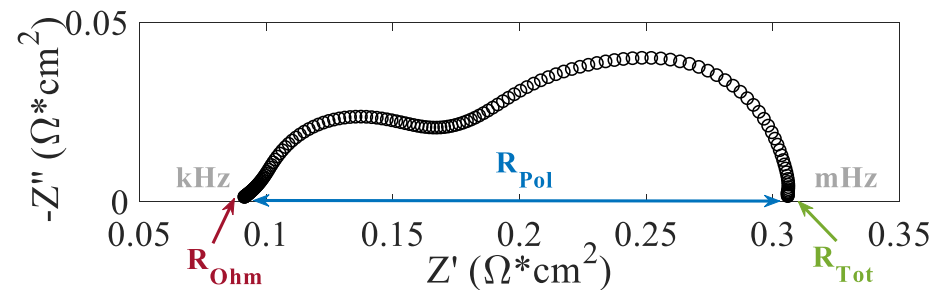


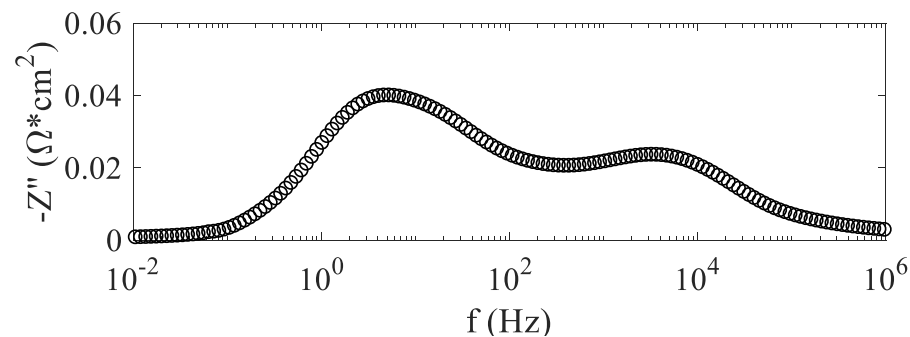
Fig. 6. EIS measurements for CoCrMo alloy during polarisation at  $-0.1$  V after different time intervals in buffered  $0.14$  M NaCl (pH 7.4,  $37^\circ\text{C}$ ). Open-circuit potential before measurement:  $-610$  mV.

# DRT approach & tool

Nyquist plot

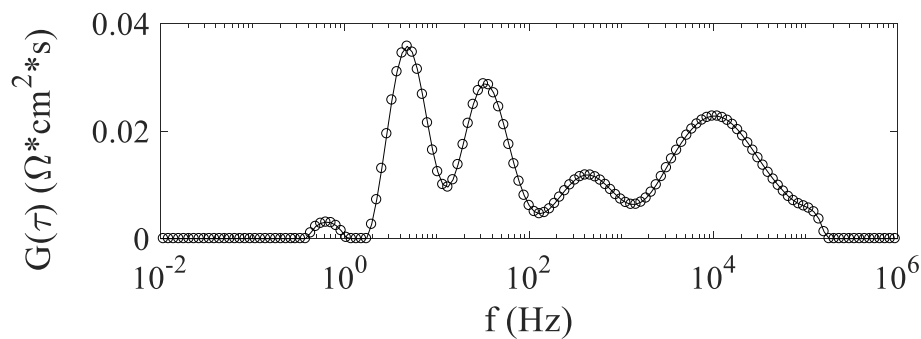


Imaginary Bode plot

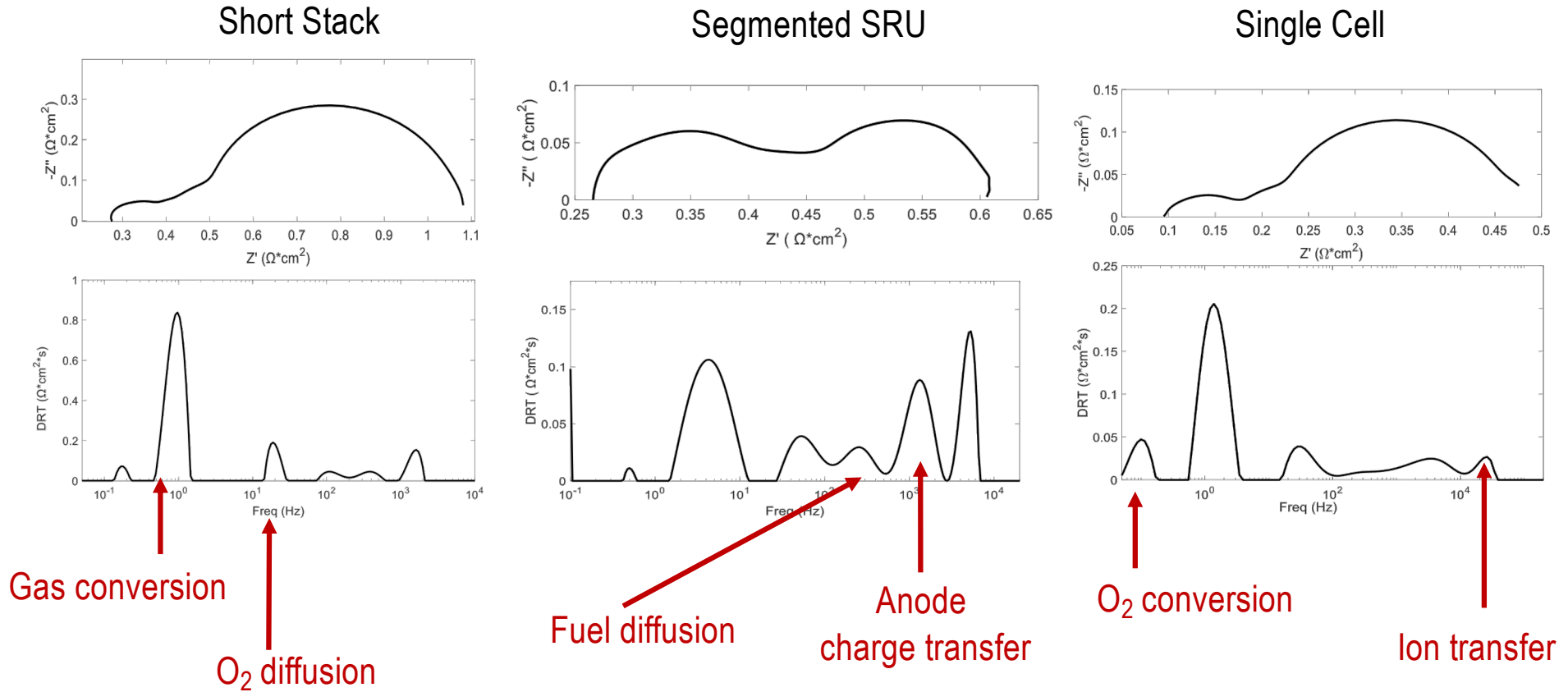


DRT plot

Distribution of Relaxation Times

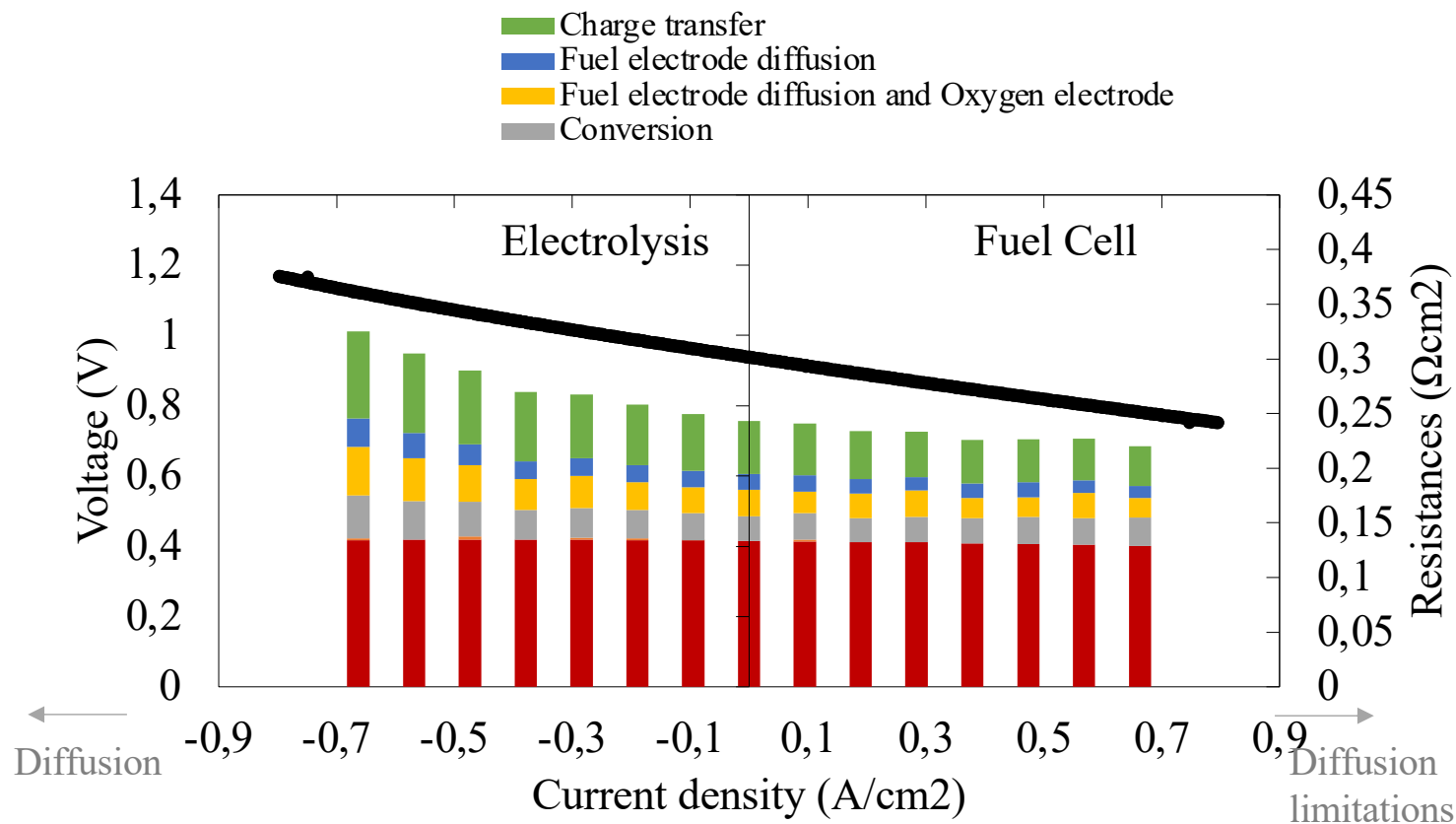


# EIS-DRT consistent in different test configurations



The same 6 processes in similar frequency regimes determined in different test configurations

# Process identification



*PhD Thesis EPFL Priscilla Caliandro 2018*



# SEGMENTED CELL OPERATION

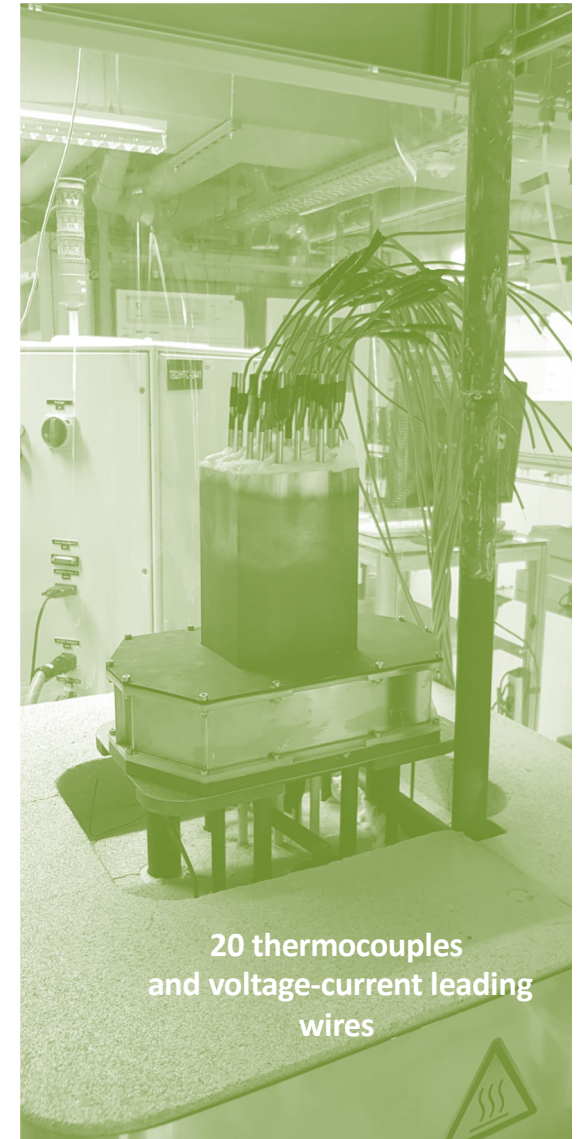
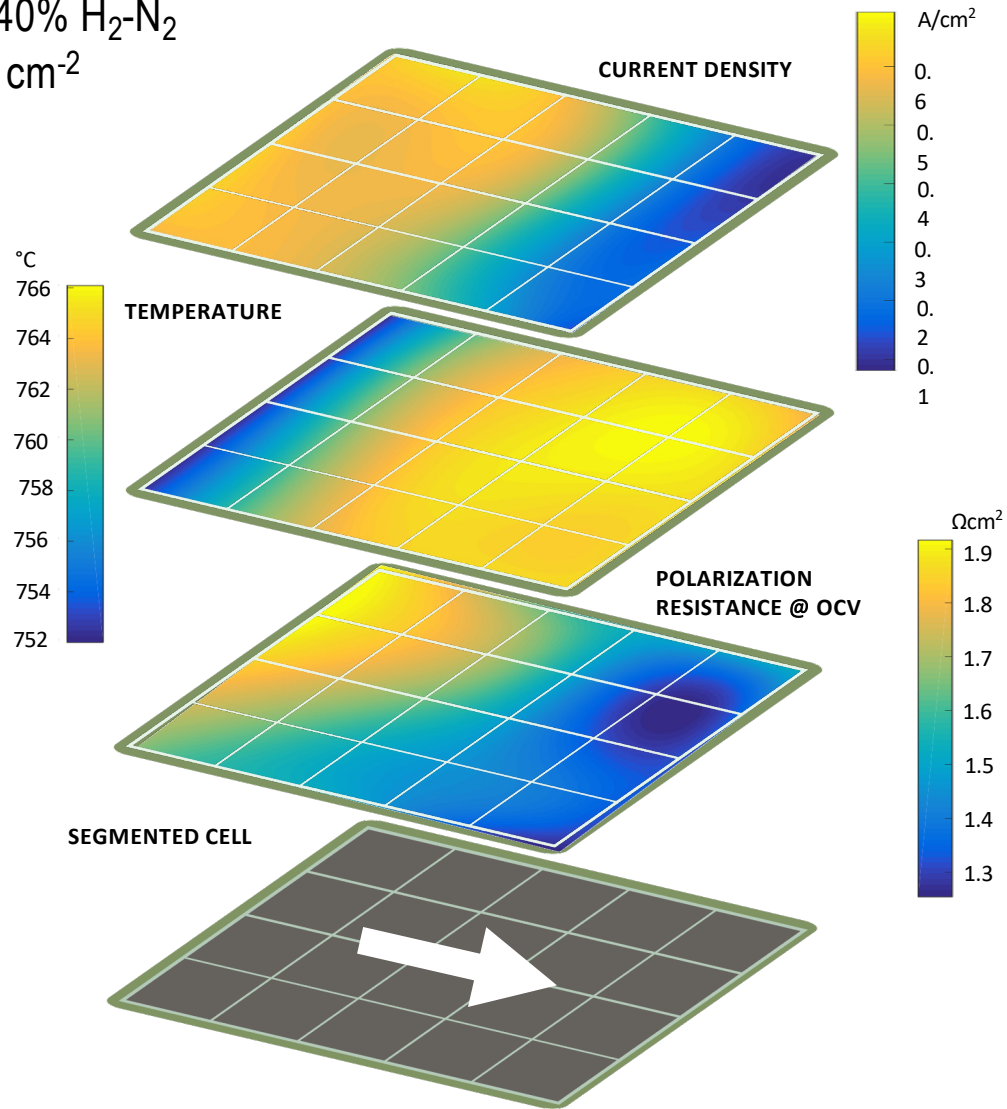
Co-flow configuration

Fuel composition 60-40% H<sub>2</sub>-N<sub>2</sub>

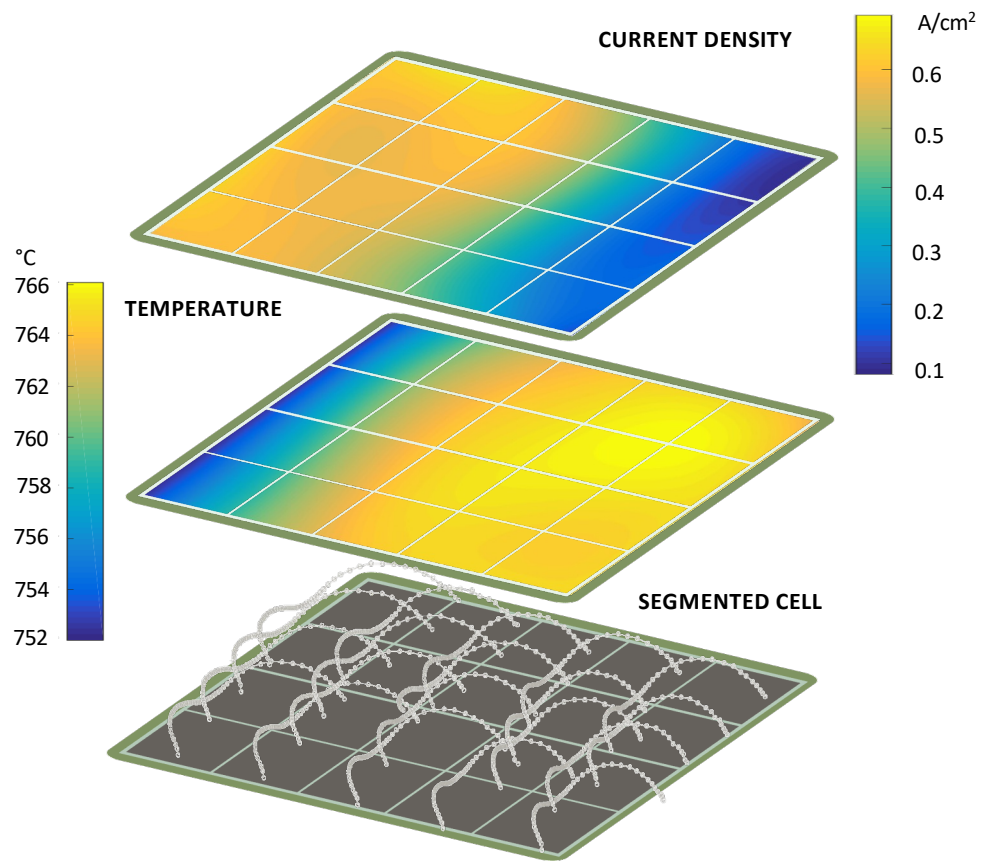
Fuel flow 5 Nml min<sup>-1</sup> cm<sup>-2</sup>

Total current 33 A

Voltage 0.65 V



20 thermocouples  
and voltage-current leading  
wires



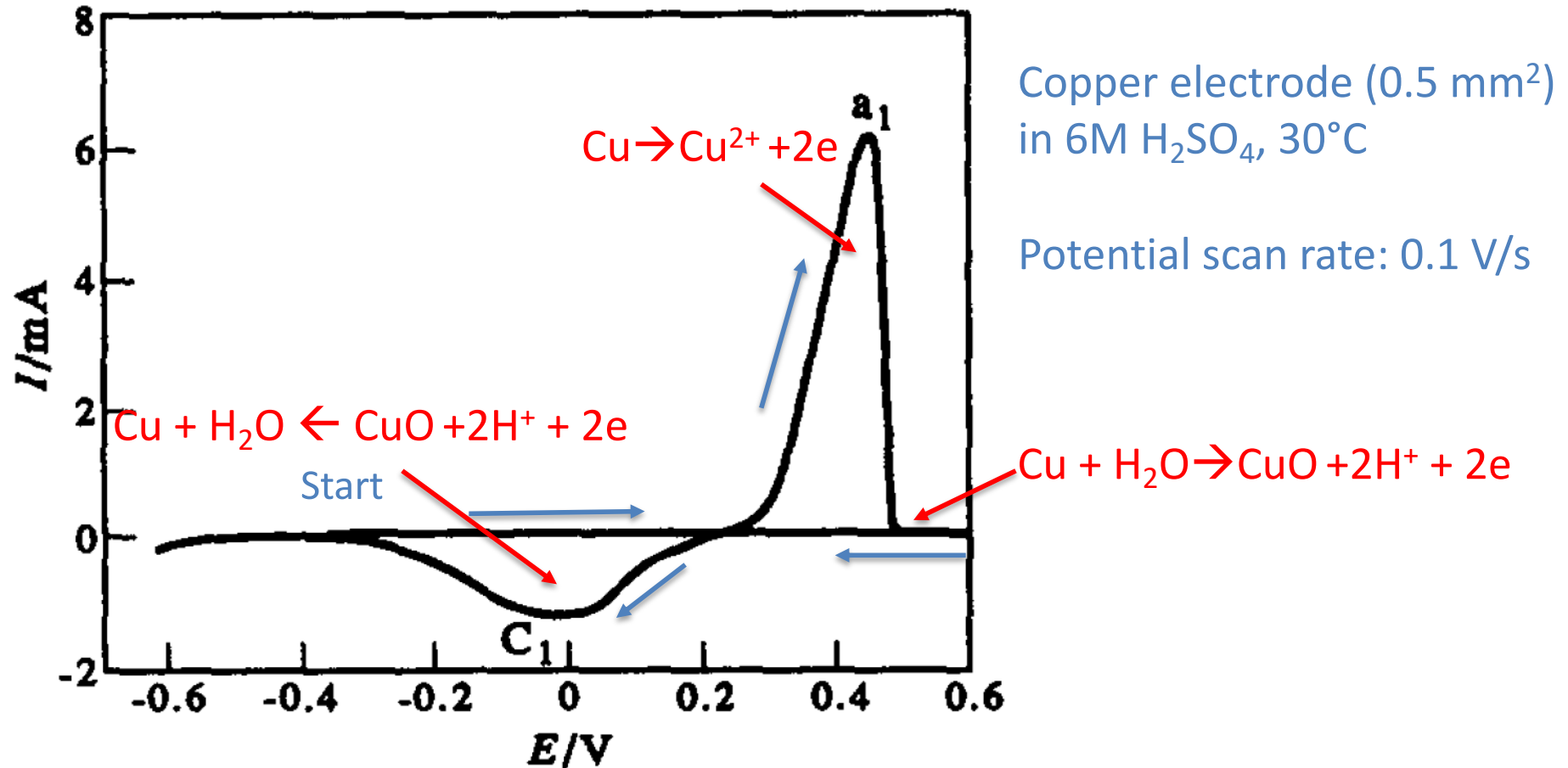
Impedance plot on each segment



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# Cyclic voltammetry (fast reversed potential scan)



Electrochemical behaviour of copper electrode in concentrated sulfuric acid solutions  
A.H. Moreira, A.V. Benedetti, P.L. Cabot, P.T.A. Sumodjo